

Technical Note N-1392

ANTIFOULING MARINE CONCRETE

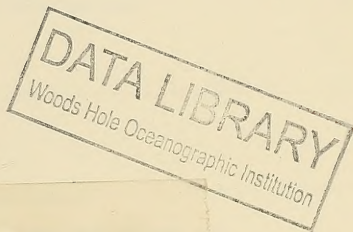
By

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May 1975

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1. Degradation

2. Materials

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CONTENTS

	Page
INTRODUCTION	1
MATERIALS	2
Lightweight Expanded Shale Aggregate	2
Portland Cement	2
Antifouling Chemicals	2
METHODS	2
Impregnation of Expanded Shale Aggregates	2
Mixing the Antifouling Concrete	3
Casting the Concrete Test Specimens	3
EXPOSURE SITES	6
Point Mugu Pier	6
Port Hueneme Harbor	6
Shallow-Water Test Site	7
SEACON Test Site	7
Guantanamo Bay, Cuba	7
EXPERIMENTAL RESULTS	8
Retention of Chemical Solution in Aggregates	8
Compressive Strength Tests	8
Shear Strength Tests	10
Antifouling Tests	10
Six-Hundred-Foot Depth	10
One-Hundred-Twenty-Foot Depth	11
Near-Surface Exposure at Guantanamo Bay	12
Near-Surface Exposure at Point Mugu	12
Near-Surface Exposure at Port Hueneme	12
Summary of Antifouling Tests	13
CONCLUSIONS	20
REFERENCES	21

LIST OF ILLUSTRATIONS

	Page
Figure 1. Concrete panel for antifouling tests.	5
Figure 2. Concrete cubes for compressive strength tests	5
Figure 3. Laminated concrete panels for shear test.	6
Figure 4. Concrete panels mounted for ocean tests	7
Figure 5. Control panel after 8 months in harbor	14
Figure 6. Control panel after 3 years in harbor	14
Figure 7. Temporary growth on panel before antifouling chemicals had oozed to the surface, in ocean 6 months	15
Figure 8. Same panel free of fouling 3-1/2 years later	15
Figure 9. Panel impregnated with TBTO mixture at a level of 250 ml per liter, after 3 years in ocean	16
Figure 10. Panel impregnated with 100% creosote, after 3 years in ocean	16
Figure 11. Smooth side of panel impregnated with 10% TBTO mixture, after 3 years in ocean	17
Figure 12. Rough side of panel impregnated with 10% TBTO mixture, after 3 years in ocean	17
Figure 13. Antifouling panel with smooth top and bottom, after 2 years in ocean	18
Figure 14. Panel impregnated with copper naphthenate mixture, after 3 years in ocean	18

LIST OF TABLES

Table 1. Numbering System and the Chemical Solutions Used to Treat Expanded Shale Aggregates for These Tests	4
Table 2. Results of Compression Tests on 2-Inch Cubes of Experimental Antifouling Concrete	9
Table 3. Shearing Forces Required to Remove 3-Inch-Square Panels of Antifouling Concrete From Concrete Surface to Which They are Bonded	11
Table 4. Compressive Strengths and Antifouling Properties of Concrete Impregnated With Various Chemical Mixtures	19

INTRODUCTION

At Navy establishments, many of the structures that must be wholly or partly immersed in the ocean are made of concrete [1]. These include wharfs, piling, seawater intakes for desalination plants and power stations, floating docks and barges, LST landing ramps, undersea platforms, and numerous other structures. After prolonged exposure in the sea, the concrete structures usually become covered with a dense growth of marine organisms. Over 2,000 species of plants and animals have been identified in the fouling community [2]. Mussels, barnacles, oysters, tubeworms, bryozoans, sea squirts, kelp, and brown algae are some of the organisms most frequently found. Once they become attached, the sessile fouling organisms are difficult to remove. They must be removed by sandblasting or scraping.

Fouling growth interferes with the function of many concrete marine structures. Most notably, fouling organisms interfere with the operation of desalination plants and coastal power stations [3]. Dense marine growth in concrete intake pipes interferes with the flow of seawater. Fouling growth in the condenser tubes reduces their heat-transferring capacity and dislodged mussels often block the tubes. Fouling organisms on the surface of concrete structures are hazardous to Navy divers. The sharp edges of calcareous barnacles may cut the skin or tear the suits of divers who brush against them. Furthermore, fouling is unsightly; and by its shear bulk, it can restrict the usefulness of almost any waterfront structure, including an increase in weight and reduction of the freeboard of floating structures.

The objective of the investigation described in this report was to develop a concrete that would resist the attachment of fouling organisms for long periods of exposure in the ocean. A concrete was sought that could not only be used as the primary construction material but that could also be used as a protective antifouling covering for purposes such as lining a concrete intake pipe [4]. It was visualized that the lining would be replaced when its antifouling properties had been depleted.

The approach chosen was to prevent the attachment of fouling organisms to concrete by means of toxic chemicals. Several problems were encountered. Merely brushing chemical agents on the surfaces of the concrete would not be adequate because the agents would soon be washed off. Impregnating concrete with toxic chemicals is next to impossible once the cement has set. Adding a toxic mixture to the cement and aggregate before they have been mixed might interfere with the curing of the concrete, especially if the toxic agent is an oil.

In the investigation at the Civil Engineering Laboratory (CEL), the method employed to incorporate mixtures of creosote and other toxic chemicals into concrete was to first impregnate a porous expanded shale aggregate with the chemicals. The impregnated aggregate was then mixed with portland cement and water to produce an antifouling concrete. This report describes the CEL investigation on antifouling concrete.

MATERIALS

Lightweight Expanded Shale Aggregate

Expanded shale aggregates are porous and lightweight and are normally used to make lightweight structural concretes which are used extensively in building construction [5]. A mixture of equal weights of 1/4- and 3/8-inch aggregates was used to make the antifouling concrete panels for the investigation described in this report.

Portland Cement

The American Society for Testing Materials (ASTM), Type III, portland cement [6] was used to make the antifouling concrete panels for the investigations described in this report. Type III cement (high early strength cement) provides high strength in a short period (usually a week or less), and the forms can be removed in about 24 hours.

Antifouling Chemicals

Creosote oil conforming to Federal Specification TT-C-645A, Class III [7], which is normally used for preserving marine timbers, was the basic chemical impregnate for the antifouling concrete. Various toxic chemicals (see Table 1) were added to the creosote oil or used separately to impregnate the porous aggregate.

METHODS

Impregnation of Expanded Shale Aggregates

The following procedure was employed to impregnate the dry porous aggregates with the experimental antifouling chemical solutions:

- (1) A fifty-fifty mixture of 1/4- and 3/8-inch aggregates was weighed.
- (2) The aggregate mixture was placed in a container and covered with the experimental antifouling chemical solution.

(3) A vacuum of 25 inches of mercury was alternately applied and released until all of the air in the porous aggregates was replaced by the antifouling solution. The saturated aggregates were allowed to stand immersed in the solution for another 6 hours.

(4) The aggregates were suspended on a screen and drained for several hours to remove excess chemical solution from their surfaces. In most of the tests, additional solution was removed from the surfaces of the aggregates by dipping them briefly in volatile mineral spirits. The aggregates were then usually permitted to stand, sometimes in an oven or in front of a fan, until the mineral spirits had evaporated.

(5) Finally, the impregnated aggregates were reweighed to determine the uptake of chemical solution.

Mixing the Antifouling Concrete

Several preliminary tests were made to determine which ratios of cement, water, and impregnated aggregates produced the strongest concrete panels. On the basis of those tests, the following procedure was adopted: a mixture was made from 0.45 part of water, one part of portland cement, and one part of impregnated shale aggregate, based on the weight of the dry aggregate before it had been impregnated.

Casting the Concrete Test Specimens

The 1- by 6- by 12-inch test panels (Figure 1) were made by pouring the concrete mix into a wooden mold lined with a thin polyethylene film. The plastic lining eliminated the need to apply grease, oil, or other mold-release agent to the interior surface of the wooden mold. A thin coating of grease or oil on the surface of the test specimen might have interfered with the exposure tests. The upper surfaces of the wet concrete in the mold were leveled with a trowel, but the upper surfaces of the finished specimens were not as smooth as the bottom surfaces which were formed in contact with the smooth bottom of the mold.

A few antifouling concrete panels with smooth tops and bottoms were made in a special mold open only on one edge. The two broad faces of the mold and all but the top edge of the mold were lined with a polyethylene plastic film. The mold was suspended vertically, resting on one edge. The concrete mix was then poured into the open edge.

Two-inch concrete cubes (Figure 2) were made from the same concrete mix from which the test panels were cast. The cubes were cast in a three-compartment metal mold described in ASTM designation C109-63 [8].

For the shear test, 1- by 3- by 3-inch blocks (Figure 3) were cast upon the surface of previously cured, untreated concrete panels. After hardening, the 1- by 3- by 3-inch blocks were sheared from the surfaces of the untreated concrete panels.

Table 1. Numbering System and the Chemical Solutions
Used to Treat Expanded Shale Aggregates for
These Tests

System No.	Chemical Solution	Quantities Mixed	System No.	Chemical Solution	Quantities Mixed
1	Tributyltin oxide	1,000 ml	9	Creosote oil	900 ml
2	Creosote oil	1,000 ml		Tributyltin oxide	100 ml
3	Water	1,000 ml		Tributyltin fluoride	5 gm
	Malachite green (water soluble)	3 gm		Pentachlorophenol	10 gm
4	Malachite green (water soluble)	3 gm		Malachite green (water soluble)	1 gm
				Malachite green (oil soluble)	1 gm
5	Creosote oil	750 ml	10	Creosote oil	900 ml
	Tributyltin oxide	250 ml		Tributyltin oxide	100 ml
	Malachite green (water soluble)	3 gm		Pentachlorophenol	10 gm
				Malachite green (water soluble)	1 gm
6	Water	1,000 ml		Malachite green (oil soluble)	1 gm
	Quaternary ammonium compound	10 gm	11	Copper naphthenate oil (in petroleum—2% copper)	1,000 ml
7	Creosote oil	900 ml	12	Creosote oil	500 ml
	Tributyltin oxide	100 ml		Copper naphthenate oil (in petroleum—6% copper)	500 ml
	Malachite green (water soluble)	20 mg	13	Creosote oil	734 ml
	Malachite green (oil soluble)	20 mg		Copper naphthenate oil (in petroleum—6% copper)	166 ml
	Pentachlorophenol	50 mg		Tributyltin oxide	100 ml
8	Creosote oil	745 ml	14	Distilled water (control)	1,000 ml
	Tributyltin oxide	250 ml			
	Nicotine	5 ml			
	Malachite green (water soluble)	50 mg			
	Malachite green (oil soluble)	50 mg			
	Pentachlorophenol	50 mg			



Figure 1. Concrete panel for antifouling tests.

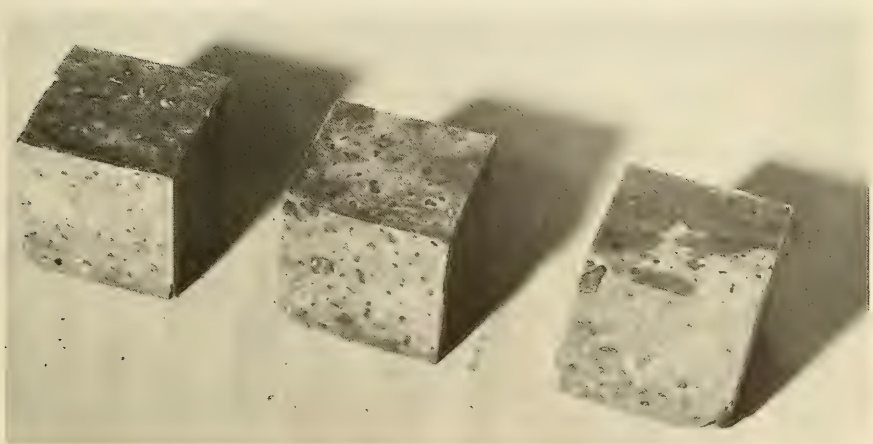


Figure 2. Concrete cubes for compressive strength tests.

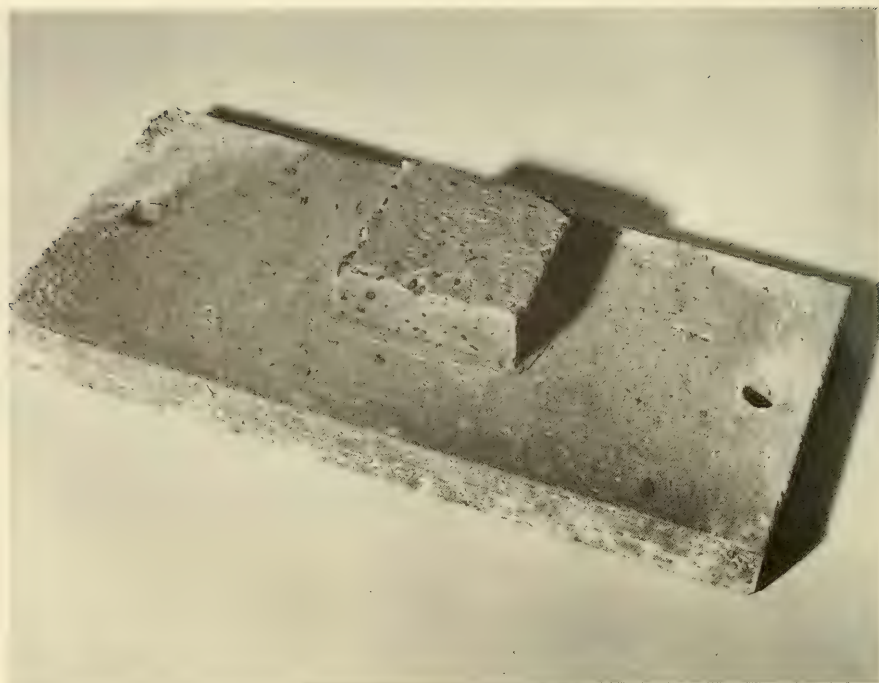


Figure 3. Laminated concrete panels for shear test.

EXPOSURE SITES

For the evaluation test specimens were exposed in the sea at five locations.

Point Mugu Pier

At Point Mugu, CA, the test panels were secured to a 10-foot-long aluminum-alloy test rack (Figure 4) and lowered into the sea from the corrosion dock at the end of a 400-foot-long pier facing the open sea. The test specimens were suspended approximately 3 feet below low-tide level. At high tide, the water depth at this location is about 25 feet.

Port Hueneme Harbor

The test panels were submerged in the harbor water from the CEL corrosion dock at Port Hueneme, CA. They were suspended approximately 2 to 3 feet below low-tide level by means of plastic rope.



Figure 4. Concrete panels mounted for ocean tests.

Shallow-Water Test Site

The shallow-water test site is located about 4 miles southwest of Port Hueneme, California, in 120 feet of water. A Submersible Test Unit (STU) was emplaced on the seafloor at this depth in December 1967 for study of fouling and biodeterioration of material [9]. The concrete test specimens were secured to the frame of the STU by Navy divers. Periodically, test specimens were recovered by divers for inspection by the project scientist.

SEACON Test Site

The SEACON Test Site [10] is located about 25 miles from Port Hueneme, in the Santa Barbara Channel in 600 feet of water. The concrete test specimens were lowered to the ocean floor at the SEACON site.

Guantanamo Bay, Cuba

Test specimens were exposed from a pier and also in a pump pit of a desalinization plant located at Guantanamo Bay to determine what effect toxic chemicals have on the attachment of fouling organisms to concrete exposed in tropical waters.

EXPERIMENTAL RESULTS

Retention of Chemical Solution in Aggregates

After the lightweight, expanded shale aggregates were saturated with a chemical solution under vacuum and then drip-dried (or washed in mineral spirits), they were found to have absorbed chemical solution to the extent of about 25 to 30% of their dry weight. It was calculated that the toxic chemical mixture constituted 10 to 12% of the weight of the antifouling concrete made from the impregnated aggregate.

Compressive Strength Tests

The results of compressive strength tests [8] conducted on 2-inch-cube concrete specimens containing chemically impregnated expanded shale aggregates are presented in Table 2. For comparison, the table shows that the compressive strengths of specimens of concrete made with sand and gravel were approximately 6,000 psi. The compressive strengths of specimens of concrete made from expanded shale aggregate impregnated with water only (System 14) or with an aqueous solution of a toxic chemical (Systems 3, 4, and 6) were approximately 5,000 psi. In nearly all instances, values of approximately 3,500 psi were obtained for concrete specimens made from aggregates impregnated with tributyltin oxide (TBTO) (System 1), creosote (System 2), or with mixture containing creosote, TBTO, and other toxic chemicals (Systems 5, 7, 8, 9, and 10). Considerably lower values were obtained for the compressive strengths of concrete made from aggregates impregnated with mixtures containing a petroleum oil (Systems 11, 12, and 13).

Rupture of the concrete cubes made from the expanded shale aggregates occurred when the bond between the cement paste and the aggregate was broken. None of the aggregate particles were observed to be sheared or crushed. It is likely that a better bond was obtained between the cement paste and natural aggregates than between the paste and the expanded shale aggregates because the surfaces of the natural aggregates are rougher and more irregular and the surfaces of the other aggregates are fire-polished. The lower compressive strengths of concrete made from the aggregates impregnated with creosote or other oils were probably due to the formation of a thin oily layer over the surface of the expanded shale aggregates which reduced bonding to the cement paste.

Various techniques for removing the oily film on the surface of the impregnated aggregates were tried. When the aggregates were drained on a screen for a brief period, too much creosote or other oil was left on the aggregate surface to permit satisfactory bonding to the cement paste. The compressive strength of concrete made from the aggregate was low. However, draining the aggregates for 24 hours removed sufficient oil from the aggregate surface to permit satisfactory bonding to the cement paste. A brief rinsing with a volatile solvent, such as mineral spirits, noticeably cleaned the surfaces of the aggregates. In some instances, but not in all, inadequate drying of the solvent before mixing the concrete appeared to impair the strength of the concrete.

Table 2. Results of Compression Tests on 2-Inch Cubes of Experimental Antifouling Concrete

System No.	Liquid Vehicle	Method for Removing Oil From Surface of Aggregate	Number of Cubes Tested	Average Compression Strength \pm Maximum Deviation (psi)
1	TBTO	Rinsed with solvent and dried.	3	3,700 \pm 1,000
1	TBTO	Rinsed with solvent and not dried.	3	2,600 \pm 1,000
2	Creosote	Rinsed with solvent and dried.	3	3,600 \pm 100
2	Creosote	Rinsed with solvent and not dried.	3	2,700 \pm 100
3	Water	Aqueous treatment. No oil.	3	4,700 \pm 400
4	Water	Aqueous treatment. No oil.	3	4,900 \pm 500
5	Creosote and TBTO	Rinsed with solvent and dried.	3	3,400 \pm 400
5	Creosote and TBTO	Rinsed with solvent and not dried.	3	2,100 \pm 200
6	Water	Aqueous treatment. No oil.	3	4,800 \pm 400
7	Creosote and TBTO	Rinsed with solvent and dried.	15	3,700 \pm 400
7	Creosote and TBTO	Rinsed with solvent and not dried.	14	3,200 \pm 700
8	Creosote and TBTO	Rinsed with solvent and dried.	6	3,500 \pm 400
9	Creosote and TBTO	Rinsed with solvent and dried.	6	3,500 \pm 800
9	Creosote and TBTO	Rinsed with solvent and not dried.	3	3,600 \pm 200
9	Creosote and TBTO	No rinse. Drained overnight.	9	3,700 \pm 400
10	Creosote and TBTO	Rinsed with solvent and dried.	17	3,700 \pm 600
10	Creosote and TBTO	No rinse. Drained 1 hour.	3	2,500 \pm 100
10	Creosote and TBTO	No rinse. Drained 4 hours.	3	3,000 \pm 100
10	Creosote and TBTO	No rinse. Drained 24 hours.	3	3,500 \pm 100
11	Petroleum	Rinsed with solvent and dried.	3	1,800 \pm 100
11	Petroleum	No rinse. Drained few minutes.	3	0
12	Creosote and Petr	Rinsed with solvent and dried.	3	1,100 \pm 100
13	Creosote and Petr	Rinsed with solvent and dried.	6	1,400 \pm 100
14	Water	Controls. Treated with water only.	14	5,300 \pm 300
14 ^a	Water	Sand and gravel treated with water only.	3	6,300 \pm 300

^a All entries but this one used 50:50 mixture of 1/4-inch and 3/8-inch aggregate.

Values of 3,500 psi in the compressive strength test are considered satisfactory for certain purposes. Thus, even though the results of the tests indicate that the antifouling concrete is weaker than most structural concrete, it would be an acceptable material for construction requiring no more than 3,500-psi compressive strength.

Rather coarse expanded shale aggregates of 1/4- and 3/8-inch mesh sizes were employed in making the antifouling concrete panels that were evaluated in the CEL investigation. No sand was employed. It is well known that concrete made with aggregates of mixed sizes ranging from fine to coarse is stronger than concrete made with only a coarse aggregate. Also, the addition of river sand improves the strength of an expanded shale concrete. It should be possible to markedly increase the strength of the CEL antifouling marine concrete by employing both fine and coarse impregnated expanded shale aggregate and by employing some unimpregnated river sand.

Shear Strength Tests

If the antifouling concrete is to be employed as a protective covering over existing concrete structures made of portland cement and gravel, it must adhere to previously cured concrete. Attempts were made to cast 1- by 3- by 3-inch blocks of the antifouling concrete on the surfaces of previously cured concrete panels made of Type III portland cement and gravel (Figure 3). Some difficulty was encountered in securing a bond, especially with the controls. The small blocks cracked loose when the molds were removed. This problem was overcome, and several control specimens and several test specimens were successfully bonded and tested. The results are given in Table 3.

The shear tests indicate that a layer of concrete made from portland cement and a porous shale aggregate impregnated with an oily mixture of creosote and toxic chemicals can be bonded to a previously cured concrete base. However, considerable care and skill are required for bonding together two layers of any portland cement concrete.

Antifouling Tests

The effectiveness of the antifouling concrete panels was tested at various sites in the ocean. Tests were made at depths of 120 and 600 feet in the ocean a few miles off shore from Port Hueneme. Tests were also made near the surface at Point Mugu, Port Hueneme, and Guantanamo Bay, Cuba. The bulk of the tests and the longest term tests were performed in the harbor at Port Hueneme, but tests at the other sites confirmed the universal effectiveness of the antifouling concrete.

Six-Hundred-Foot Depth. The tests at a depth of 600 feet were conducted in the vicinity of the STU structure, an ocean-bottom rack or frame on which numerous devices and materials were fastened for ocean exposure tests. The STU structure was emplaced on the seafloor in the Santa Barbara Channel at a depth of 600 feet. The antifouling concrete panels exposed at the STU site were made of porous aggregate impregnated

Table 3. Shearing Forces Required to Remove 3-Inch-Square Panels of Antifouling Concrete From Concrete Surface to Which They are Bonded

System No.	Liquid Vehicle	Method for Removing Oil From Surface of Aggregates	Load (lb)
2	Creosote	Rinsed with solvent not dried.	1,700
9	Creosote and TBTO	Rinsed with solvent and dried.	1,400
9	Creosote and TBTO	Rinsed with solvent and dried.	2,200
10	Creosote and TBTO	Rinsed with solvent and dried.	1,200
10	Creosote and TBTO	Rinsed with solvent and dried.	1,500
11	Petroleum	Rinsed with solvent and dried.	1,000
14	Water	Controls. No oil to remove.	1,500
14	Water	Controls. No oil to remove.	2,600
14	Water	Controls. No oil to remove.	2,500

with a mixture of creosote, tributyltin oxide (TBTO) at the 100-ml-per-liter level, malachite green, and pentachlorophenol (System 10). Control panels in which the aggregate was impregnated with water (System 14) were also exposed at the 600-foot site. The panels were exposed for a period of 9 months. No fouling accumulated on either the test panels or the control panels. Occasionally a few fouling organisms were found on specimens of other material exposed at this station but the fouling was scant and was slow to develop.

One-Hundred-Twenty-Foot Depth. Fouling was somewhat heavier at the shallow exposure site at a depth of 120 feet. Specimens of the antifouling concrete in which the aggregates were impregnated with creosote mixtures containing TBTO at the 250-ml-per-liter level (System 8) and at the 100-ml-per-liter level (Systems 7 and 9) and with mixtures containing copper naphthenate (Systems 11, 12 and 13) were exposed at the 120-foot station. Untreated control panels (System 14) and untreated panels which were coated with a mixture of TBTO at the 100-ml-per-liter level and rubber or epoxy compound were also exposed at the 120-foot depth. The specimens were all exposed at that depth for a period of 19 months.

At the end of the exposure period, the control panels were covered by a fairly heavy layer of fouling organisms. The fouling was markedly heavier on the sheltered side than on the side exposed to the prevailing ocean currents.

There was very little fouling on the panels made with aggregates impregnated with mixtures containing TBTO at either the 100- or 250-ml-per-liter level. What little fouling there was, tended to be only on the side exposed to the prevailing ocean currents. This is the reverse of the fouling pattern on the control panels which was heaviest on the

sheltered side. A possible explanation for this difference is that the toxic chemicals were removed most rapidly from the side of the panels exposed to the current. In the absence of the toxic chemicals, the fouling organisms might thrive better in the quieter water on the side protected from the current.

The panels protected by a layer of rubber or epoxy compound containing TBTO at the 100-ml-per-liter level had less fouling than the untreated control panels but more fouling than the panels made from the aggregate impregnated with mixtures of creosote and TBTO. There was about the same amount of fouling on the panels made from aggregates impregnated with copper naphthenate mixture as there was on the control panels.

Near-Surface Exposure at Guantanamo Bay. A few panels of experimental antifouling concrete were exposed for 1 year near the seawater intake of the desalination plant at Guantanamo Bay. Panels made from aggregates impregnated with a mixture of creosote containing TBTO at the 100-ml-per-liter level (System 7) were essentially free of fouling organisms and the untreated control panels were covered by a heavy growth of fouling organisms.

Near-Surface Exposure at Point Mugu. Concrete panels made from aggregates impregnated with numerous toxic mixtures (Systems 1 through 6 and 13) were exposed near the surface at Point Mugu, California. Approximately 10 months after the first of the panels had been placed in the water, a storm destroyed the exposure rack, and all of the panels were lost. The only data on the panels was that obtained during inspections made after the panels had been in the water 3 to 8 months. In 3 months the control panels were covered by a light growth of algae, calcareous tubeworms, branching bryozoa, and hydroids, but no mussels or barnacles. In 8 months the surfaces of the control panels and the surfaces of the panels containing a quaternary ammonium compound were completely covered with a dense growth of tubeworms, encrusting and branching bryozoa, mussels, and barnacles. In 8 months concrete panels made with aggregate impregnated with 100% TBTO were covered by a light growth of bryozoa, algae, hydroids and a few barnacles. In 3 months, concrete panels made from an aggregate which was impregnated with 100% creosote and no other toxic chemical were already covered by a light growth of algae and numerous barnacles. In 8 months panels made from an aggregate which was impregnated with a creosote mixture containing TBTO at the 25% level (System 5) were free of fouling except for an occasional small barnacle. Those made with a mixture of creosote, copper naphthenate, and TBTO at the 100-ml-per-liter level (System 13) were covered by only a scanty growth of brown algae.

Near-Surface Exposure at Port Hueneme. The greatest number of tests and the longest tests were conducted from the materials test dock at Port Hueneme. Concrete panels containing no toxic chemicals were heavily covered by a dense growth of fouling organisms of all types (Figures 5 and 6). The panels impregnated with mixtures of creosote and other toxic chemicals, including TBTO at the 250-ml-per-liter level (Systems 5 and 8), were sometimes temporarily covered by light growth of

fouling before the chemicals oozed to the surface of the panel (Figure 7). The fouling was transient, however, and died off when the toxic creosote mixture reached the surface. The same panel was still essentially free of fouling organisms (Figure 8) after it had been in the ocean for 4 years. Other panels made from aggregates impregnated with a mixture of creosote and TBTO at the 250-ml-per-liter level were also essentially free of fouling growth after 3 or more years of exposure in the ocean at Port Hueneme (Figure 9). A panel treated with 100% creosote was covered by a light growth of fouling organisms at the end of 3 years (Figure 10).

The smoother side of panels made from aggregates impregnated with mixtures of creosote containing TBTO at the 100-ml-per-liter level (Systems 7, 9, and 10) were also relatively free of fouling organisms (Figure 11). The rough side of the same panels was frequently covered by a light growth of fouling organisms (Figure 12). This phenomenon occurred frequently among the toxic concrete panels. One possible explanation is that the toxic creosote mixture might have come through the smooth surface more readily than through the rough one. Also, the smooth side was the bottom side of the panel and during the setting of the concrete the toxic mixture might have tended to concentrate at the bottom of the mold.

One of the special panels made with smooth tops and bottoms was exposed in the ocean at Port Hueneme for 2 years. The aggregates from which the panel was made were impregnated with a mixture of creosote, TBTO at a level of 100-ml-per-liter, and other toxic chemicals (System 10). Except for a scant growth of brown algae, the panel was free of fouling growth (Figure 13).

Concrete panels made from aggregates impregnated with mixtures of copper naphthenate and either a volatile solvent or creosote (Figure 14) were covered by as heavy a fouling growth as the control panels containing no toxic chemicals. Coatings of either an epoxy compound or rubber containing TBTO at the 100-ml-per-liter level also failed to prevent or retard the accumulation of fouling organisms when exposed in the ocean for 3 or more years.

Summary of Antifouling Tests. Salient features of the antifouling tests on concrete impregnated with various chemical mixtures are summarized in Table 4. Mixtures of creosote and tributyltin oxide (TBTO) were the most effective of the antifouling mixtures. Malachite green, copper naphthenate, and quaternary ammonium compounds were ineffective. Comparisons of the fouling on panels exposed at the undersea station at depths of 600 and 120 feet and at near-surface exposure sites at Port Hueneme, Point Mugu, and Guantanamo Bay, disclosed that as expected, fouling is heaviest near the surface of the ocean. No comparisons were made of the relationship of compressive strength and antifouling properties.

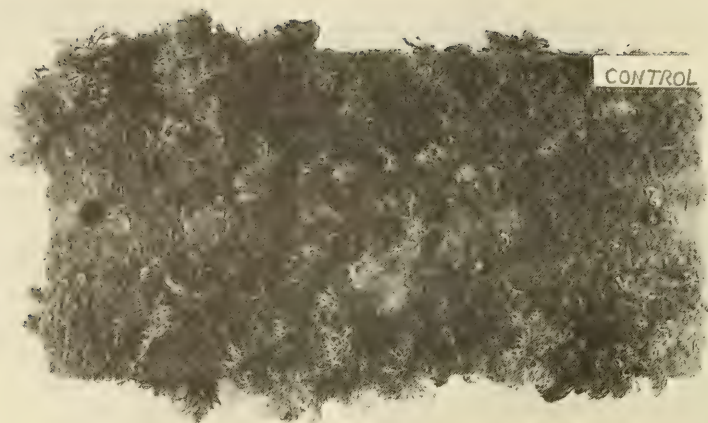


Figure 5. Control panel after 8 months in harbor.



Figure 6. Control panel after 3 years in harbor.

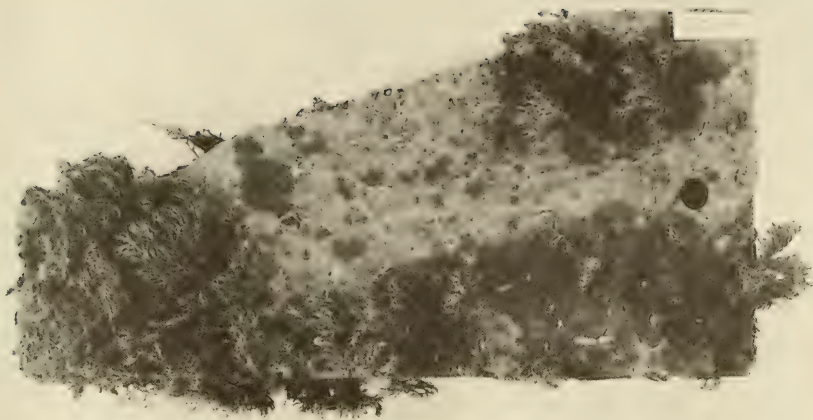


Figure 7. Temporary growth on panel before antifouling chemicals had oozed to the surface, in ocean 6 months.

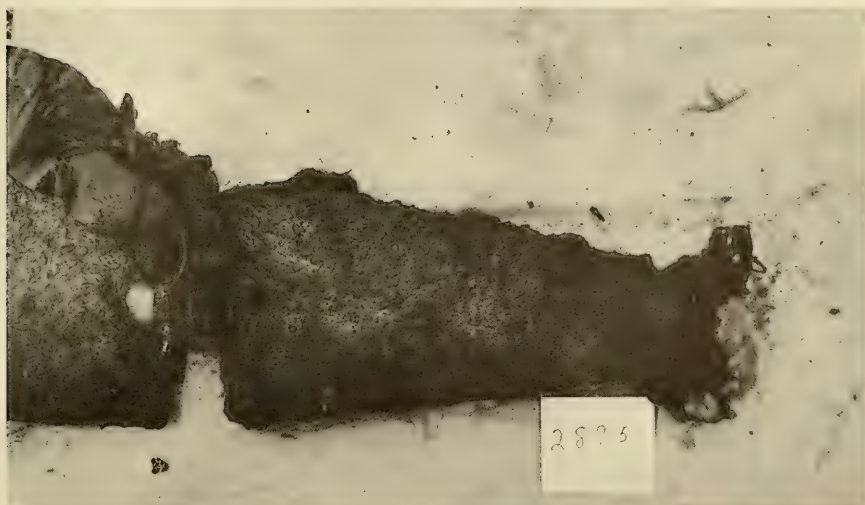


Figure 8. Same panel free of fouling 3-1/2 years later.



Figure 9. Panel impregnated with TBTO mixture at a level of 250 ml per liter, after 3 years in ocean.



Figure 10. Panel impregnated with 100% creosote, after 3 years in ocean.

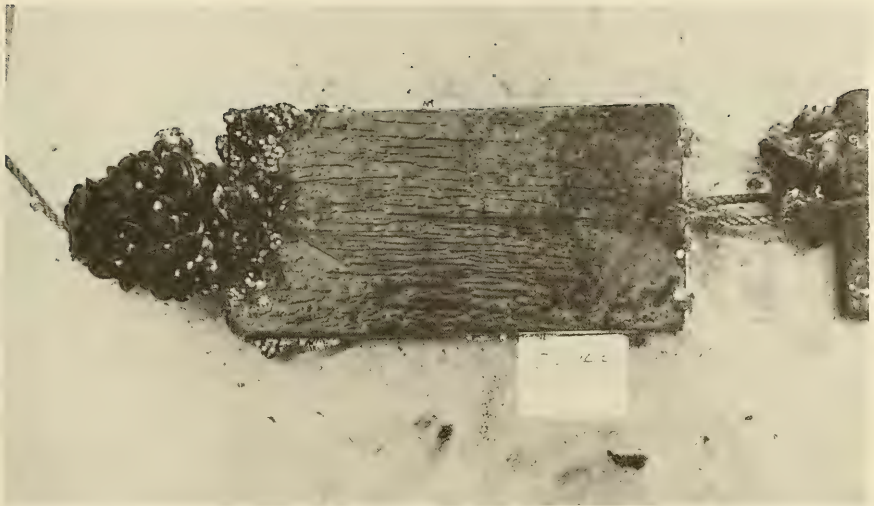


Figure 11. Smooth side of panel impregnated with 10% TBTO mixture, after 3 years in ocean.

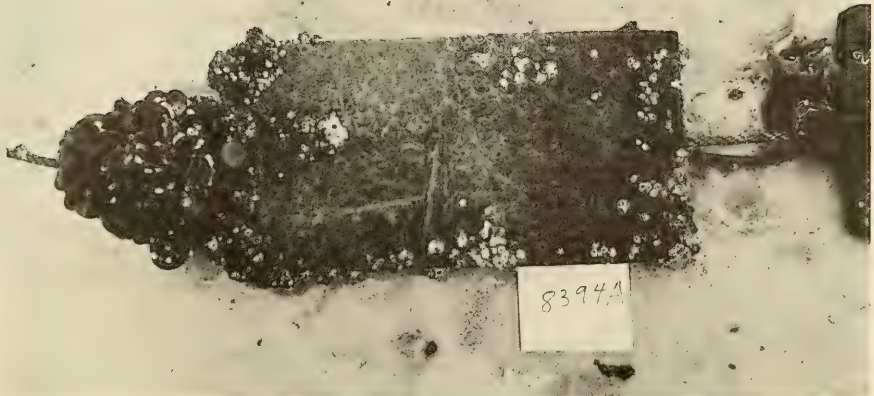


Figure 12. Rough side of panel impregnated with 10% TBTO mixture, after 3 years in ocean.

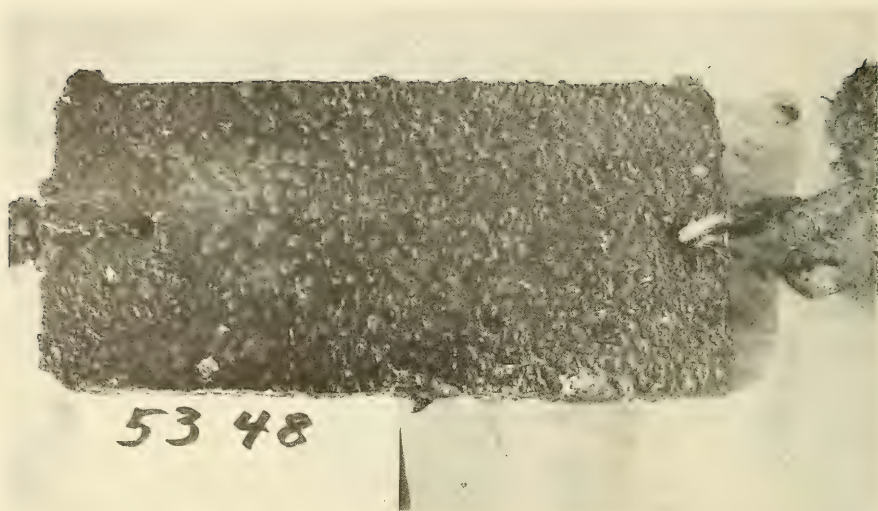


Figure 13. Antifouling panel with smooth top and bottom, after 2 years in ocean.

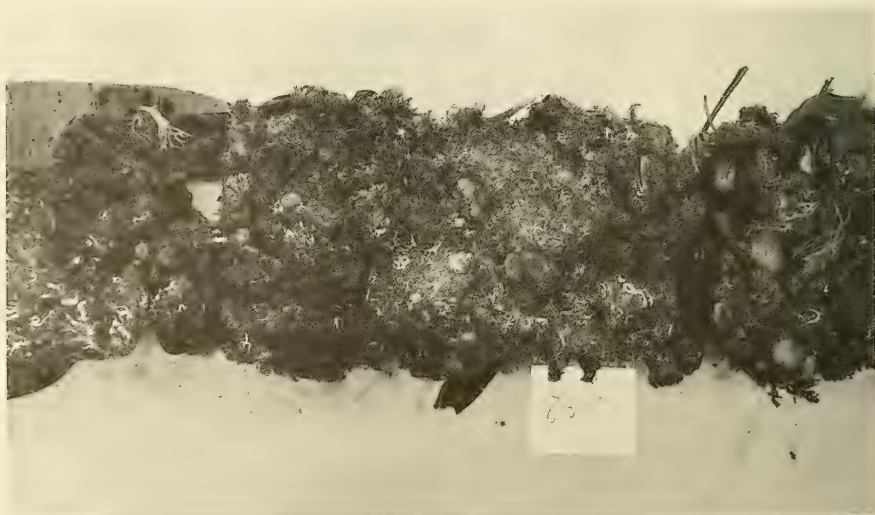


Figure 14. Panel impregnated with copper naphthenate mixture, after 3 years in ocean.

Table 4. Compressive Strengths and Antifouling Properties of Concrete Impregnated With Various Chemical Mixtures

Antifouling Chemical Mixture	Approximate Compressive Strength of Concrete (psi)	Fouling Growth After Exposures of 3 to 4 Years in the Ocean
Creosote-based mixtures containing TBTO at a level of 250 ml/liter (Systems 5 and 8)	3,500	none
Creosote-based mixtures containing TBTO at a level of 100 ml/liter (Systems 7, 9, and 10)	3,500	scant to none
Creosote only (System 2)	3,500	light
Copper naphthenate in petroleum and creosote (Systems 11, 12, and 13)	1,500	heavy
Thin film of TBTO impregnated rubber on unimpregnated concrete	5,000	heavy
Water and malachite green (System 4)	5,000	heavy
Water and quaternary amine (System 6)	5,000	heavy
Water only (System 14- the controls)	5,000	heavy

CONCLUSIONS

Antifouling marine concrete made from a porous expanded shale aggregate impregnated with mixtures of creosote, tributyltin oxide at levels of 100 to 250 ml per liter, and other toxic chemicals have remained essentially free of marine fouling for at least 4 years. The antifouling concrete is not as strong as concrete made from sand and gravel, but it is sufficiently strong for construction in which a compressive strength of 3,500 psi is acceptable. The antifouling concrete is effective at Guantanamo Bay, Cuba, as well as at Port Hueneme and Point Mugu, California. It is effective near the surface of the ocean and at a depth of 120 feet. Concrete made from aggregate impregnated with a 50:50 mixture of creosote and copper naphthenate is fouled as readily as ordinary concrete containing no toxic chemicals. Coating concrete with rubber that contains tributyltin oxide at a level of 100 ml per liter does not provide long-term protection against fouling.

REFERENCES

1. Naval Civil Engineering Laboratory. Technical Note N-1211: Antifouling concrete, Preliminary report, by James S. Muraoka. Port Hueneme, CA, Jan 1972.
2. Woods Hole Oceanographic Institution. Contribution No. 580: Marine fouling and its prevention. United States Naval Institute, Annapolis, MD, 1952.
3. H. A. Todhunter. "Special Lining in Concrete Intake Prevents Fouling from Marine Growth," Power Engineering, Nov 1966, pp 67-68.
4. U. S. Patent No. 3,784,357: Protective surfaces or liners for subaqueous structure, by James S. Muraoka, 8 Jan 1974.
5. Portland Cement Association. "Design and Control of Concrete Mixtures," Engineering Bulletin, Eleventh Edition, Jul 1968.
6. American Society for Testing and Materials. ASTM. Designation C150-73a: Standard specification for portland cement, Type III. High Early Strength.
7. Federal Specification TT-C-645A: Creosote, coal tar, Class III, technical, for treating timbers for marine use.
8. ASTM Designation C109-63: Standard method of test for compressive strength of hydraulic cement mortar--using 2 inch (50 mm) cube specimens.
9. Civil Engineering Laboratory. Technical Report R-810: Biodeterioration and fouling of materials--five years at depth of 120 feet, by James Muraoka. May 1974.
10. Joseph R. Padilla and James S. Muraoka. "Corrosion and fouling of an instrumented array at 600-foot ocean site," in Proceedings of Third International Congress in Marine Corrosion and Fouling, Oct 1972. Gaithersburg, MD, National Bureau of Standards, 1972, pp 48-60.

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